



Early Journal Content on JSTOR, Free to Anyone in the World

This article is one of nearly 500,000 scholarly works digitized and made freely available to everyone in the world by JSTOR.

Known as the Early Journal Content, this set of works include research articles, news, letters, and other writings published in more than 200 of the oldest leading academic journals. The works date from the mid-seventeenth to the early twentieth centuries.

We encourage people to read and share the Early Journal Content openly and to tell others that this resource exists. People may post this content online or redistribute in any way for non-commercial purposes.

Read more about Early Journal Content at <http://about.jstor.org/participate-jstor/individuals/early-journal-content>.

JSTOR is a digital library of academic journals, books, and primary source objects. JSTOR helps people discover, use, and build upon a wide range of content through a powerful research and teaching platform, and preserves this content for future generations. JSTOR is part of ITHAKA, a not-for-profit organization that also includes Ithaka S+R and Portico. For more information about JSTOR, please contact support@jstor.org.

WATER SOFTENING FOR MUNICIPALITIES¹

BY MILTON F. STEIN

Hardness and its causes. The presence of salts of calcium and magnesium in water give rise to peculiar physical and chemical properties collectively spoken of as hardness. It is more easily defined in terms of chemical tests than in its popular conception, which at best is rather indefinite and to a large extent relative. A traveler will readily notice the difference in this respect between the water of one town and another, whereas the residents, through habit, probably do not consider the degree of hardness of their water supply objectionable. However, if through a lapse of treatment, there is a small rise in hardness in the water of a town accustomed to softened water, vigorous protests are heard at once.

Of the more general properties constituting hardness the failure to lather promptly stands first. This results in an undue consumption of soap and patience and in the formation of an insoluble lime curd, disagreeable to the skin in personal use, and rendering clothing greyish, streaked and stiff in laundry operations. Then there is the scaling in boilers, kettles and hot water pipes. The author also believes that hard water has a taste, or at least is less agreeable to drink than soft water. The individual constituents have special characteristics which should be briefly noted.

a. Calcium and magnesium bicarbonates are very similar in properties. They are very soluble in water, increasingly so with rising temperature up to about 170° F., where decomposition commences, with the formation of carbonic acid and normal carbonates, the latter, relatively insoluble, being precipitated. Hence, these two salts are said to cause temporary hardness, being removed by heating or boiling. Their precipitation in boilers forms soft scale.

b. Calcium sulphate is very soluble in cold water but becomes decreasingly so on heating, particularly with increasing pressure. Hence, when concentrated by evaporation in steam boilers, it soon reaches the precipitation point, and forms a hard scale, so that it is

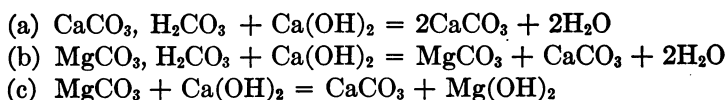
¹Read before the Illinois Section on March 25, 1919.

bound to be troublesome even if present in small quantities, unless the boilers are frequently blown off, which is both troublesome and expensive.

c. Magnesium sulphate is not only very soluble in cold water, but becomes increasingly so on heating, and therefore does not itself form scale. It hinders the lime-softening process, however, combining with lime to form the objectionable calcium sulphate. Under high boiler pressures it will combine with any calcium carbonate present, resulting in a double precipitate of magnesium carbonate and calcium sulphate.

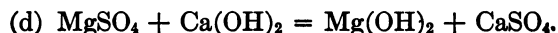
d. Calcium and magnesium chloride are the least important of the hardening constituents. Being extremely soluble, they do not cause trouble by incrustation.

The process of water softening. On adding slacked lime to a hard water, the following reactions take place:



In equation (a), the calcium carbonate formed is only soluble to the extent of about 13 p.p.m. and so precipitates out. The magnesium carbonate in equation (b), being soluble to the amount of about 100 p.p.m., remains in solution to that extent, and requires additional lime for its removal as the insoluble hydroxide. At least this is the theory, but in practice such ideal conditions do not obtain. The solubility of the calcium carbonate as precipitated from a solution seems to be greater than the amount which can be dissolved by shaking it in the powdered form with water. The presence of magnesium carbonate affects the solubility of calcium carbonate, as there appears to be a definite limit to the combined solubility of the two salts. The presence of other compounds, particularly sodium chloride, tends to increase these residual solubilities, and they are also affected by the temperature of the water. The magnesium hydroxide in equation (c), forms very slowly and is apt to assume a colloidal condition, and to return to its former state by absorbing carbonic acid from the air.

If either the sulphate or chloride of magnesium is present a further reaction takes place:—



As will be seen, this consumes lime uselessly, since the calcium sulphate formed is the most troublesome kind of permanent hardness, and the magnesium hydroxide will probably remain in colloidal solution.

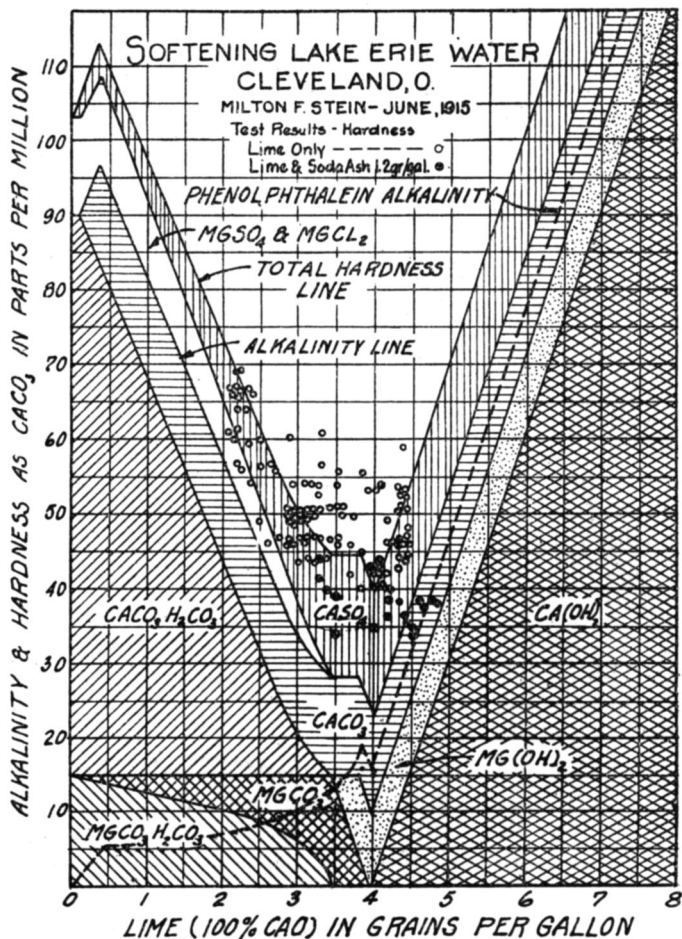


FIG. 1

In figure 1 are shown graphically some of the results of an investigation on softening Lake Erie water at Cleveland, Ohio. This diagram shows the ultimate composition of the water after treatment with various amounts of lime, and on the assumption of a very

long reaction period. The vertical scale gives alkalinity and hardness as parts per million of calcium carbonate. The horizontal scale shows the amounts of lime added, in grains per gallon. It shows that the hardening constituents of this water consist of 15 p.p.m. magnesium bicarbonate, 75 p.p.m. calcium bicarbonate (these, combined, giving the water an alkalinity of 90 p.p.m.) and magnesium sulphate and chloride to the extent of 13 p.p.m., making the total hardness 103 p.p.m. Treatment with approximately half a grain of lime results in an increase of hardness, since the calcium carbonate formed is less than the saturation value and remains in solution. Larger quantities of lime result in progressively decreasing hardness. It will be observed that the lime reacts with the hardening constituents in proportion to their amounts, and that only that part of the lime which combines with the calcium bicarbonate does effective work, since in the case of magnesium bicarbonate, the soluble mon carbonate is formed, and the magnesium sulphate is replaced by the more objectionable calcium sulphate. By adding as much as 4 grains of lime some of the mon carbonate of magnesium can be precipitated as the hydroxide, in theory at least, while more than 4 grains causes an increase in hardness again. A judgment based on this diagram would place the optimum amount of lime at about 3 grains, which was borne out by the results of numerous large scale tests at the Cleveland experimental plant.

Lake Erie water lends itself particularly to such a diagrammatic representation because of its constant composition. For most waters, a series of diagrams or a model would be necessary, owing to variation of the constituents.

The rate of reaction in water-softening is quite slow. Some experimental results obtained with Cleveland water are shown in figure 2. The dots show the results of five tests run, using $2\frac{1}{2}$ grains per gallon of lime and with a water temperature of 20°C. The methyl orange and phenolphthalein alkalinities were determined by titration at short intervals. The arrangement of the points shows that a very definite law governs the course of the reaction. From the determinations and supplementary tests it is possible to surmise what is happening, as shown by the shaded areas. One point of interest not brought out by the main diagram becomes evident on plotting the logarithms of the values, as shown by the smaller diagram. There is a very evident break in the continuity, slope and curvature of the line at a point corresponding to log. alkalinity =

4.1, or alkalinity = 60. This suggests that the reaction is taking place in two steps, first, the reaction of the lime with the calcium salts; second, with the magnesium salts. The same thing may be noticed in connection with the soap test as applied to water con-

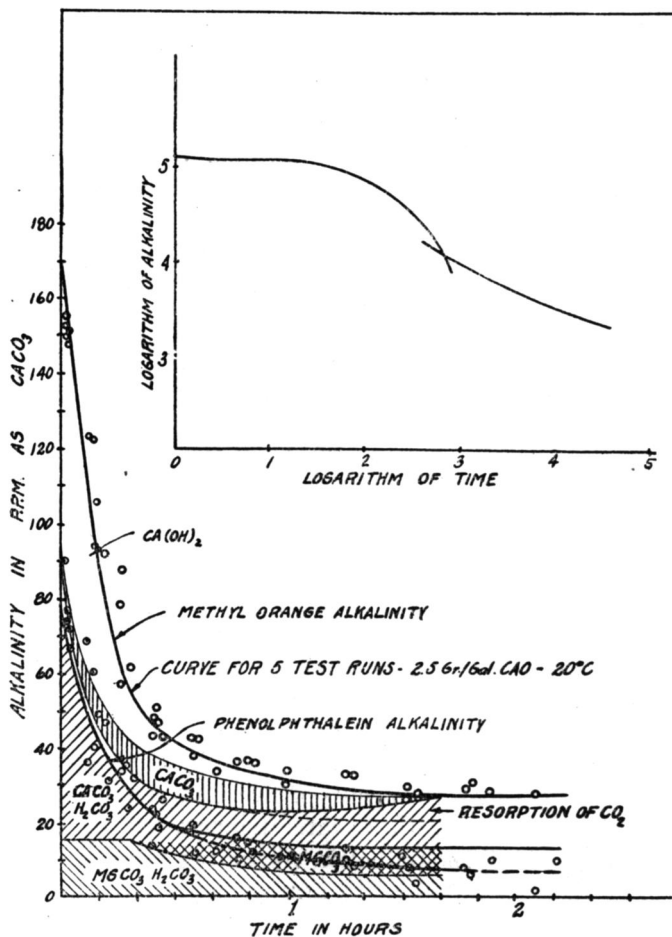
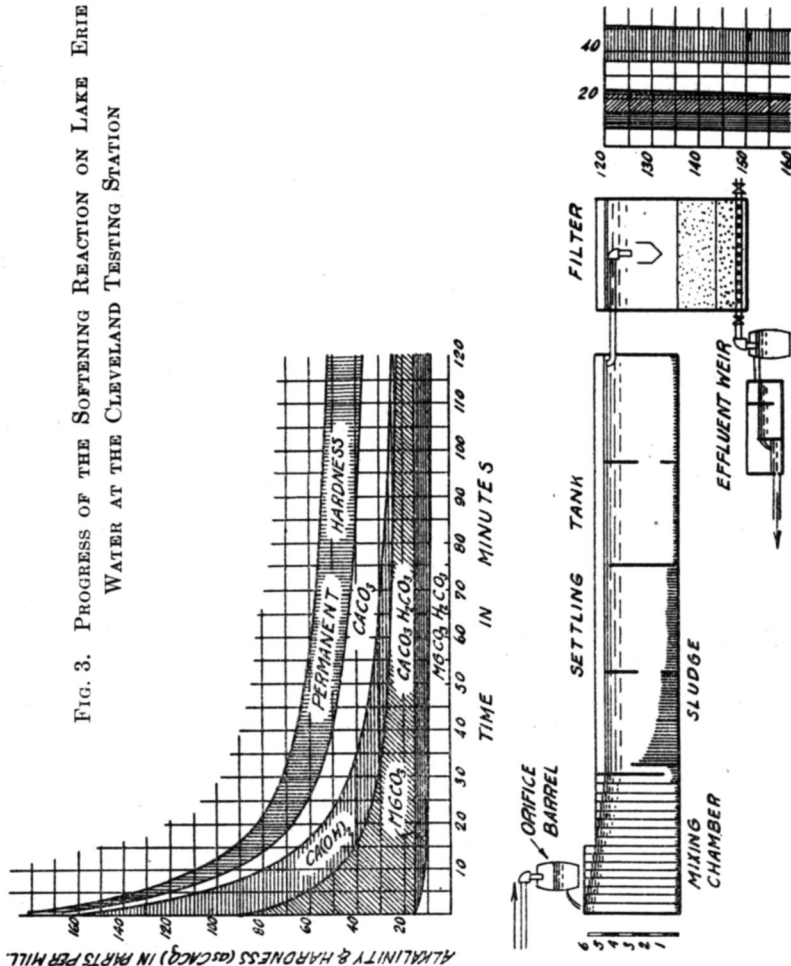


FIG. 2. RATE OF REDUCTION IN SOFTENING LAKE ERIE WATER

taining both calcium and magnesium compounds. There is a false end point when the calcium compounds have been displaced, followed later by the true end point when the reaction with the magnesium salts is completed. In all cases the magnesium compounds seem to be more sluggish in action.

Figure 3 shows the progressive softening reaction which took place in the Cleveland testing plant. The incoming water was measured by an orifice barrel, the lime solution being proportioned to it by a

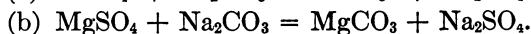
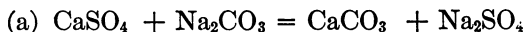


float operated device. It then passed through an up-and-down mixing chamber into a settling tank. The depth of sludge deposit in the settling tank is indicated. From the settling tank it passed

through a mechanical filter of the usual type. There was usually a drop in alkalinity in passing through the filter, due to the precipitation of colloidal magnesium hydroxide and probably calcium carbonate by contact with the sand, as well as to a continuation of the softening process. There was some incrustation of the sand, as well as on plain and galvanized iron plates which were exposed continuously for 5 months in a stream of the softened and filtered water. This question of after-deposits is a serious one, and requires special study in individual cases. It causes trouble in the filter sand, underdrains, controllers, in meters, if galvanized inside, and in house plumbing. It is much more pronounced if the attempt is made to carry the softening to the limit than if a margin of safety is allowed, probably stopping just short of where the magnesium reaction begins. The addition of a coagulant during the latter portion of the settling period seems to act as a preventive.

The question of temperature in connection with the reaction period should be mentioned. The temperature factor in chemical reaction velocities is still a debated point. No formula of general applicability has yet been devised. In many cases the reaction velocity doubles for every 10°C. rise in temperature. Since the data heretofore considered were obtained at about optimum temperature for large scale water softening in the temperate zone, viz.: 20°C. or 68°F., this would mean that for a four-hour reaction period, an eight-hour period must be substituted at 10°C., or a sixteen-hour period at 0°C. Besides this there seems to be a sort of inertia to the reaction starting at all in extremely cold water, which is very discouraging at times.

Nothing has been said as yet regarding the use of soda ash for removing permanent hardness. The equations are:



The reaction is sluggish when carried out in the cold. When the permanent hardness is low or is due to by-products of the lime process, the amount of soda-ash required is small and according to the law of mass action, the rate of reaction will be very slow. The magnesium carbonate formed in the case of magnesium salts is quite soluble and remains in solution. It will thus be seen that the use of soda ash in softening municipal water supplies is on a much more

precarious basis than in the case of boiler feed waters, and should not be entered upon without careful study and serious consideration.

The essential features of a softening plant. In the light of the foregoing and from other experience the requisites for carrying out a water-softening project successfully may be given.

1. There should be a very thorough analytical and experimental investigation which should cover particularly:

- a. Analyses of the water in question and the variations to be expected therein.

- b. The amount of reagent which can be successfully applied without causing trouble from after-deposits and incrustation. It is suggested that special attention be given to the point where magnesium reactions commence.

- c. The question of whether it is advisable to attempt the removal of permanent hardening constituents in view of the additional burden which the use of soda ash involves.

- d. The determination of the reaction period required under conditions of minimum concentrations of reagent and minimum temperature.

To interpret experimental data in terms of practical working conditions requires special experience based on contact with both phases of the problem.

2. There must be an understanding on the part of the municipal authorities that to accomplish its task a water-softening plant must be adequate throughout, and that there can be no skimping in the size of parts or in equipment or in operating expenses if satisfactory results are to be obtained. This holds more rigidly in the case of softening plants than in the case of ordinary water purification plants.

3. The principal design features of a water-softening plant should include:

- a. Mixing chambers in which the softening reagents are thoroughly dispersed through the raw water, either by mechanical devices or by baffling. This mixing action also seems to accelerate the reactions.

- b. Large settling basins whose capacity is based upon the reaction period as determined for conditions of minimum temperature. These basins will generally be several times as large as would be required or the regular type of purification plants.

- c. Means for adding a coagulant solution either at the entrance to or near the exit from the settling basins, or at both points, to assist in starting and completing the softening reaction.

d. Mechanical filters of the usual type.

e. Special apparatus for properly slacking and feeding the lime solution into the water. Due to the tendency of lime emulsions to settle and to choke feed piping, this portion of the design requires particular care and study.

Special problems of the large softening plant. It is needless to give a description of the details of municipal water-softening plants of small or moderate size, since they conform so closely, except as to relative proportion of parts, to the usual type of mechanical filter plants. In the case of large installations, however, there have been certain special developments which may not be without interest.

As mentioned already, the settling basins will be quite large. The precipitate obtained will be voluminous, and special provision must be made for its frequent and expeditious removal. This requires that the settling capacity be divided into a number of units, and that at least one spare unit be provided so that cleaning will not interfere with the operation. Frequent clean-out valves must be placed in the floor of the basins. In the diagram of the experimental plant it was shown that at least three-fourths of the sludge collected in the first few feet of the settling tank, in fact it occasionally happened that this portion of the tank almost filled up in a week's time. It appears to the author that the first quarter-length of the settling basins should be made deeper than the remainder and equipped with automatic sludge removers of the continuous type, such as Dorr thickeners.

Since the sludge is composed essentially of the lime added to the water and an equal amount abstracted from the water, both in the form of calcium carbonate, it has been suggested that this sludge be reburned, thus recovering not only the lime added but an equal amount in addition. Mr. C. P. Hoover tried this experimentally at Columbus on a considerable scale, and small-scale experiments were made at Cleveland. The product is about 75 per cent water-soluble CaO , and slakes readily. The author made some preliminary studies for such a lime recovery plant, which included resettling tanks, special centrifugals and rotary kilns fired with producer gas. The estimated cost of reburned lime is about 75 per cent of that for commercial lime, based on available CaO . The reburning plant is quite a separate institution, requiring operators with a different type of training and experience. It is a manufacturing proposition, and this from present experience, does not lend itself readily to munici-

pal control. For this reason, and because the product is less easily handled, the advantages and disadvantages seem very evenly balanced.

Perhaps the most interesting phase of a large water-softening installation is the handling of the large quantity of chemicals used. Thus the Cleveland plant, operated at its capacity of 150,000,000 gallons daily, would require about 40 tons of lime per day. The arrangement of the chemical house is shown in figure 4. The lime arrives in box cars by way of a depressed siding on one side of the building. It is shoveled into a chute by power shovels, and falls into a crusher. The crushed lime is carried by elevator and screw conveyers to overhead storage bins, which have a capacity of 1500 tons of lime. Each four bins connect into one daily hopper and from this the lime flows by gravity to automatic scales.

The discharge of the scales can be automatically controlled to conform to the pumpage of raw water by means of the Venturi meter in the raw water line which passes through the chemical house. Figure 5 is a diagram of this device. From the raw water meter piezometer pipes lead to float tubes in the usual manner, the difference in head actuating differential gears, cams, etc., so that the resulting movement is directly proportional to the flow through the meter. A cord, with counterbalance to take up slack, transmits this movement to a traveling carriage *abcd*, which can move backward and forward on the rollers *r, r, r, r*, over an aluminum friction disc driven at constant speed by a synchronous motor. Mounted on the carriage is a small contact wheel. With no flow, the position of the carriage brings this wheel to the center of the disc, where it does not revolve. As the flow increases the carriage shifts and the contact wheel moves faster and faster. At each revolution this wheel closes an electrical contact, which, through suitable relays, actuates the automatic scales, causing them to discharge. These scales are really equal arm balances although entirely disguised by auxiliary levers, housing, and other complications. As soon as a scale is tripped, the automatic discharge gate opens and the lime flows out very quickly. This unbalances the scale beam, which tilts up, and in so doing closes the discharge and opens the feed gate. The feed gate, of the under-cut type, is gradually closed as the scale pan fills up and closes entirely when the predetermined amount has been reached. The scale is then ready to be tripped again by the contact wheel.

The scales discharge into slaking tanks, where the lime is slaked

with hot water, and agitated by motor-driven paddles. The slacked lime overflows into solution tanks where it is cooled and diluted with water, and is then pumped into the raw water.

The coagulant, either ferrous sulphate or alum, is handled in a similar manner, with minor modifications.

The Cleveland work was designed and built under the direction of R. Winthrop Pratt, consulting engineer, Frank H. Stephenson, designing engineer, Robert Sharp Jones, constructing engineer; the author being in immediate charge of the design of the portions

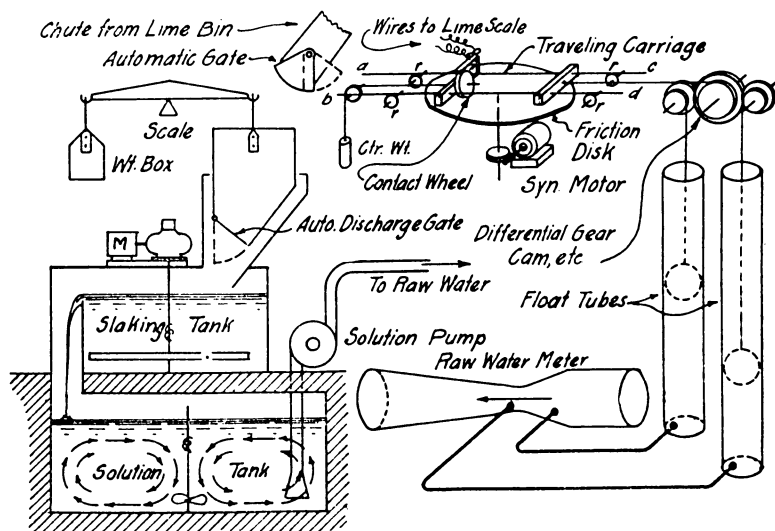


FIG. 5. LIME FEED CONTROL

herein described. The automatic scales were furnished by the Richardson Scale Company. The proportional feed device was built by the Builders' Iron Foundry, from sketches furnished by the author.

DISCUSSION

M. F. STEIN: In reply to questions the author stated that the rate of reaction should not be very different if a greater proportion of magnesium were present. The lime will react with both the calcium and magnesium bicarbonate in proportion to the amounts of these two present, but the magnesium carbonate as it is formed will

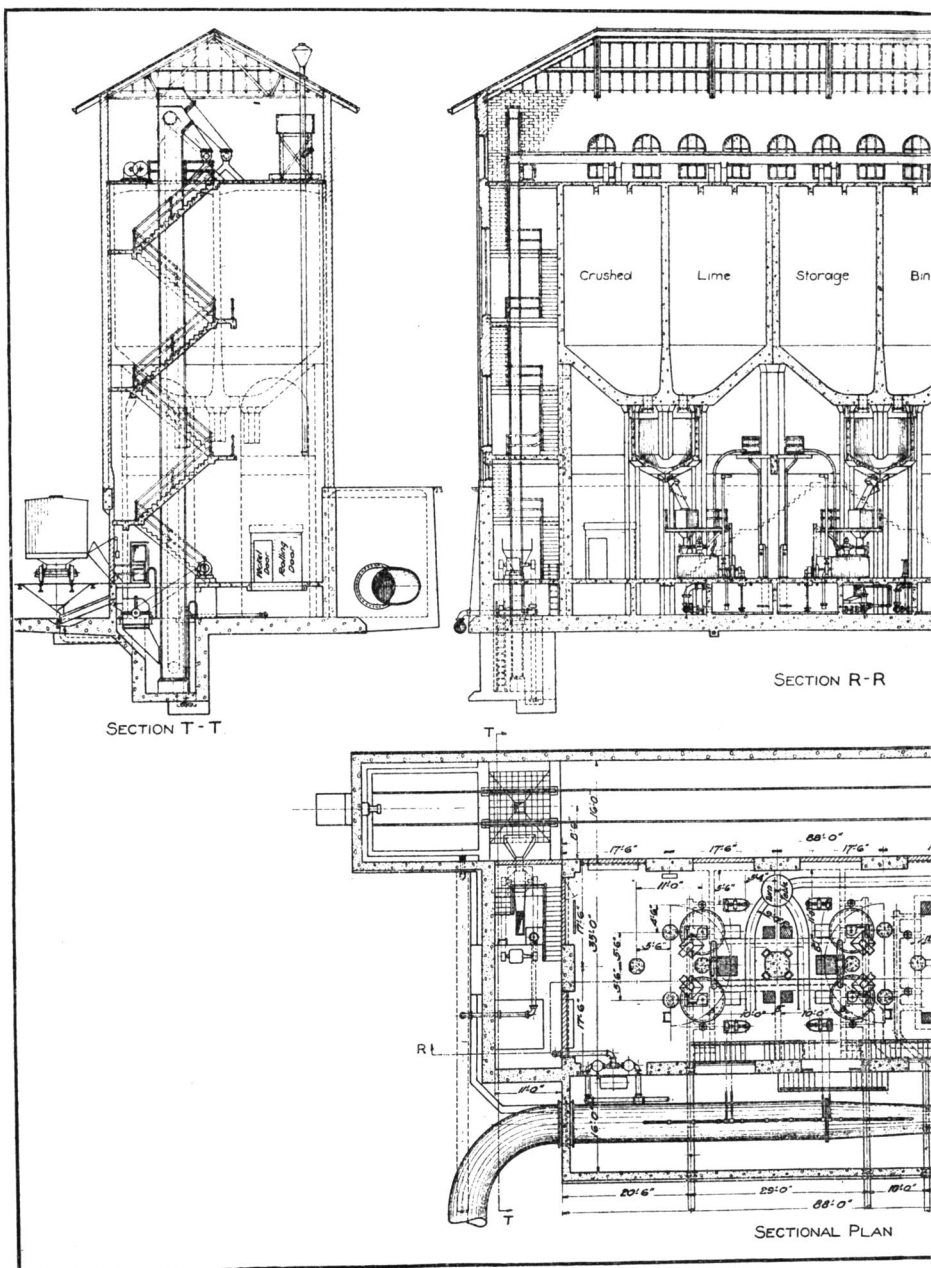
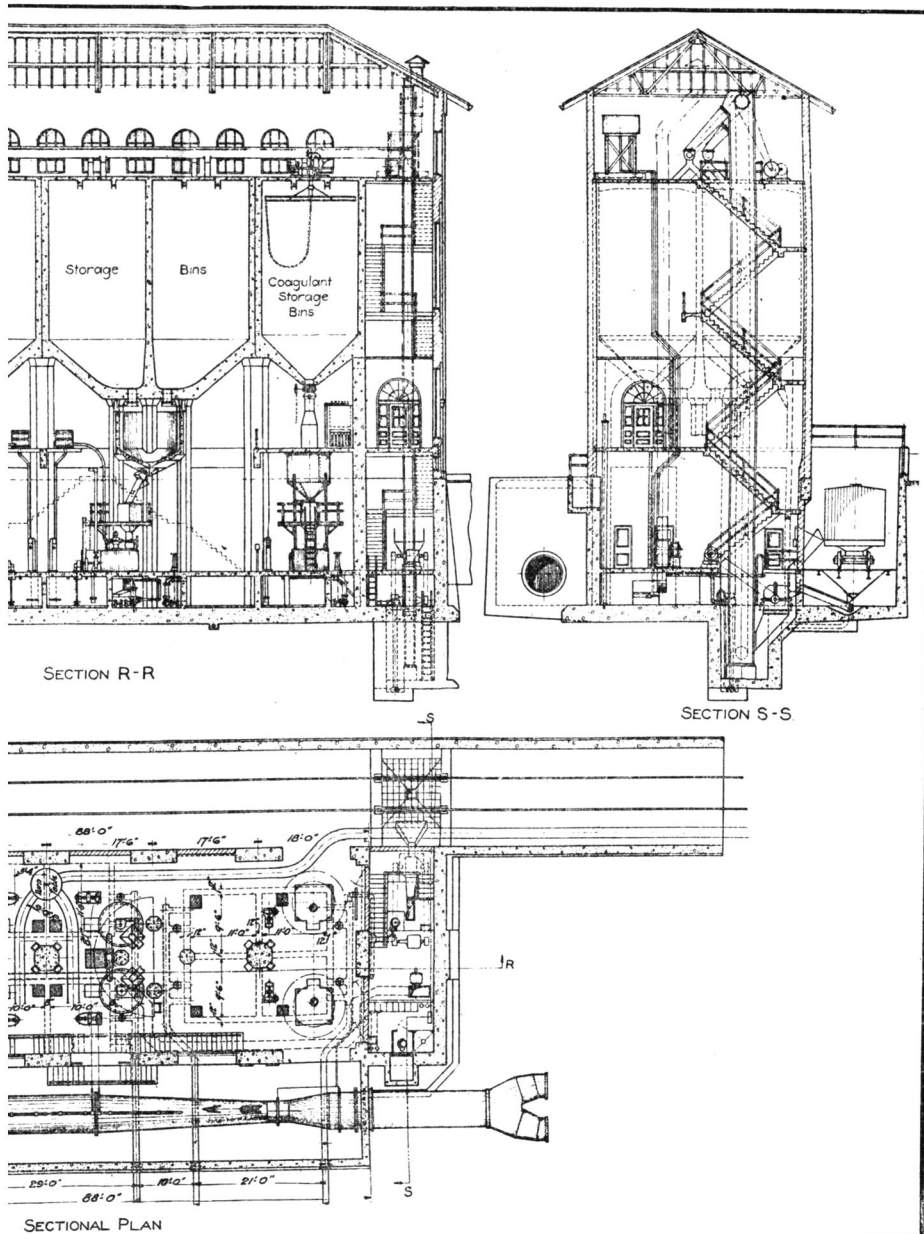


FIG. 4. CHEMICAL HOUSE, CLEVELAND



HOUSE, CLEVELAND FILTRATION PLANT

probably absorb some of the carbonic acid from the calcium bicarbonate, so that it would not be precipitated until the calcium bicarbonate had all been precipitated, but the rate of reaction would be essentially the same for any combination of the two salts, (this is more or less hypothetical).

A low temperature would slow up the reaction; the lower the temperature the slower the reaction.

If there were a superabundance of magnesium rather than calcium the magnesium would probably stay in solution in a colloidal form to quite an extent, more so at a low temperature than at a higher temperature. If there were more colloidal matter present, the calcium carbonate would tend to bring about a precipitation of the colloidal material by simple contact effect.

The experiments were run long enough to show that under carefully controlled conditions there is always a small amount of after-deposit. It was found that by restricting the dose to 3 grains of lime, or less, and not using soda ash it was practicable to cut down deposits to a negligible quantity.

There were bicarbonates present. In the lower part of the settling tank there would be carbonates present. After the water passed through the filters, and especially after it stood in the clear water tank a while, a certain amount of absorption would change some of the carbonates back into the bicarbonates.

There has been no trouble with bridging of the line in any part of the apparatus below the bin gates. There was sometimes bridging, or rather arching, just above the gates. In the scales the trouble was not very pronounced. With very fine, partly hydrated lime, the feed gates would not always shut off completely. Some of the lime would dribble in, hydrated lime flowing almost like water.

W. F. MONFORT: Scales of that kind sometimes overflow and deliver 2 or 3 bushels at a time. With hydrated lime there might be anywhere up to 200 pounds of fine material discharging from the scales at each operation.

M. F. STEIN: The scales discharged about every twenty minutes while the author was there. He left soon after the plant was put in operation. No softening had been attempted with the large plant, owing to lack of labor and other conditions. The author could not recall just how often the scales were figured to dump when the plant

is running, but believes it was about once every two minutes, for full capacity operation.

No attempt is made to warm the water by utilizing the heat from the lime slakers. Some of the details were taken from the St. Louis plant, because the same make of scale was used in both cases. The details for slaking the lime and heating the water are different.